

Technical University of Denmark



Ultrabroadband time-resolved THz spectroscopy of polymer-based solar cells

Cooke, David G.; Krebs, Frederik C; Jepsen, Peter Uhd

Published in:

Proceedings of the 1st International Symposium on Terahertz Nanoscience (TeraNano 2011) and 2nd Workshop of International Terahertz Research Network (GDR-I THz 2011)

Publication date:
2011

Document Version
Early version, also known as pre-print

[Link back to DTU Orbit](#)

Citation (APA):

Cooke, D. G., Krebs, F. C., & Jepsen, P. U. (2011). Ultrabroadband time-resolved THz spectroscopy of polymer-based solar cells. In Proceedings of the 1st International Symposium on Terahertz Nanoscience (TeraNano 2011) and 2nd Workshop of International Terahertz Research Network (GDR-I THz 2011)

DTU Library
Technical Information Center of Denmark

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Ultrabroadband time-resolved THz spectroscopy of polymer-based solar cells

David G. Cooke

Physics Department, McGill University, Montreal, Canada H3A 2T8

Frederik Krebs

Risø National Laboratory for Sustainable energy, Technical University of Denmark, DK-4000 Roskilde, Denmark

Peter Uhd Jepsen

DTU Fotonik, Technical University of Denmark, DK-2800 Kongens Lyngby, Denmark

Abstract—We have developed ultrabroadband THz spectroscopy in reflection mode for characterization of conductivity dynamics in conductive polymer samples used in organic solar cells. The spectrometer is designed to have a time resolution limited only by the duration of the optical pump pulse, thus enabling the investigation of charge generation processes on the sub-100-fs time scale.

I. INTRODUCTION

Time-resolved THz spectroscopy is a very powerful tool for the investigation of ultrafast processes in condensed-matter systems [1]. It has been used for studies of carrier dynamics in a wide range of semiconducting materials, including bulk GaAs [2-3], thin films of crystalline, nanocrystalline, amorphous silicon [4], and TiO₂ [5] just to mention a few. Most studies to date have been focused on the region below 2 THz due to instrumentation limitations (electro-optic generation and detection in ZnTe crystals), and thus the nature of conductivity processes have partly been discussed on the basis of measurements of a small section of the full conductivity spectrum. Larger bandwidth measurements have proven their value in several investigations, as exemplified by references [6-8].

Here we demonstrate a time-resolved THz spectroscopy (TRTS) system which employs air plasma generation of ultrashort THz pulses [9-10] in combination with air biased coherent detection (ABCD) of the THz transients [11].

Figure 1 shows a schematic diagram of the experimental setup.

The generation and detection processes are both based on four-wave mixing in air. As in any other frequency conversion processes, the bandwidth of the process is always limited by the bandwidth of the laser source and the bandwidth of the phase matching. With air as the nonlinear medium the phase matching conditions are perfect over an extremely broad bandwidth range, and therefore the bandwidth of the generation and detection processes is in practice limited only by the laser bandwidth.

We use a transform-limited 35-fs laser pulse from a standard regenerative amplifier system (SpectraPhysics Spitfire),

resulting in THz transients with a spectral coverage from 1 to 35 THz and a THz pulse duration of less than 50 fs.

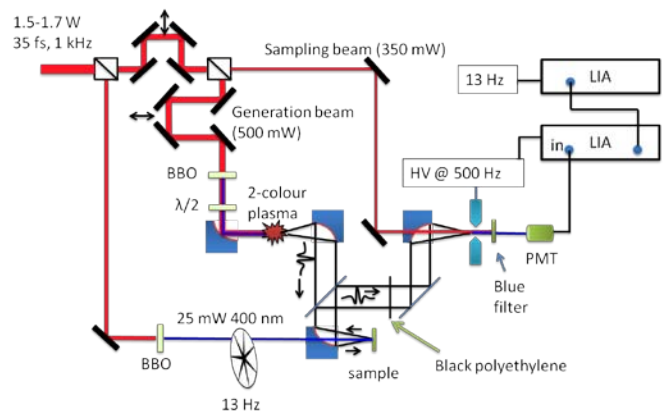


Figure 1: Schematic diagram of ultrabroadband time-resolved THz spectroscopy setup operating in normal-incidence reflection mode.

With this system we perform optical pump – THz probe spectroscopy of the evolution of the photoinduced conductivity in a roll-to-roll processed, device-ready bulk heterojunction film consisting of a blend of the conductive polymer P3HT (electron donor) and PCBM (electron acceptor) [12]. Figure 2 shows the chemical structure of P3HT and PCBM.

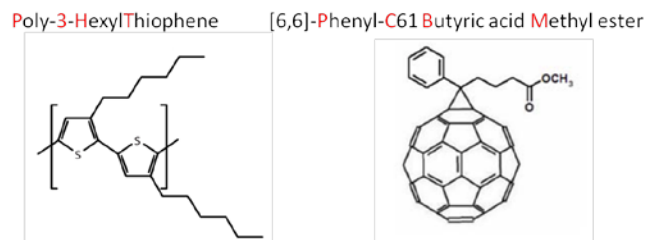


Figure 2: Chemical structure of P3HT and PCBM

The pump-probe spectroscopy is carried out with a 400-nm pump pulse (< 40 fs duration) exciting the sample at a time $\Delta\tau$ before reflection of the THz pulse. The photoinduced changes of the conductivity leads to modifications of the reflection amplitude and phase of the THz signal,

$$1 + \frac{\Delta E(\omega, \Delta\tau)}{E_{ref}(\omega)} = \frac{1 - n - Z_0 d \sigma(\omega, \Delta\tau)}{1 + n + Z_0 d \sigma(\omega, \Delta\tau)} \frac{1 + n}{1 - n} \quad (1)$$

where n is the index of refraction of the substrate, Z_0 is the free-space impedance, d is the sample thickness, and $\sigma(\omega, \Delta\tau)$ is the frequency-dependent, complex-valued photoconductivity at the pump-probe delay time.

Figure 3 shows an example of the evolution of the conductivity of the P3HT/PCBM device-ready thin film subsequent to photoexcitation [13].

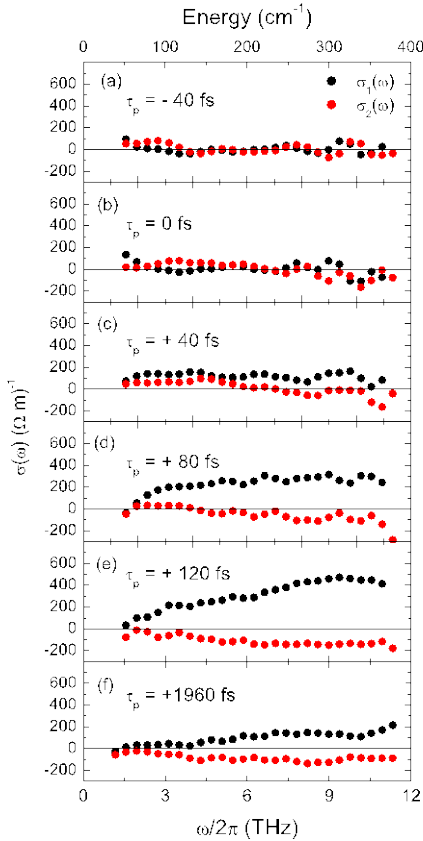


Figure 3: Short time evolution of the real (black circles) and imaginary (red circles) part of the conductivity of the P3HT/PCBM BHI film after 400-nm photoexcitation.

Initially the conductivity spectrum displays a Drude-like response, indicating mobile charges. Later, the suppression of the DC conductivity and the negative sign of the imaginary part of the conductivity show a more localized response.

ACKNOWLEDGMENTS

David Cooke acknowledges financial support from NSERC and the H. C. Ørsted Fund.

REFERENCES

- [1] P. U. Jepsen, D. G. Cooke and M. Koch, "Terahertz spectroscopy and imaging – Modern techniques and applications," *Laser Photon. Rev.* **5**, 124-166 (2011).
- [2] M. C. Beard, G. M. Turner and C. A. Schmuttenmaer, "Transient photoconductivity in GaAs as measured by time-resolved terahertz spectroscopy," *Phys. Rev. B* **62**, 15764-15777 (2000).
- [3] M. Schall and P. U. Jepsen, "Photoexcited GaAs surfaces studied by transient terahertz time-domain spectroscopy," *Opt. Lett.* **25**, 13-15 (2000).
- [4] D. G. Cooke, A. N. MacDonald, A. Hryciw, J. Wang, Q. Li, A. Meldrum and F. A. Hegmann, "Transient terahertz conductivity in photoexcited silicon nanocrystal films," *Phys. Rev. B* **73**, 193311 (2006).
- [5] G. M. Turner, M. C. Beard and C. A. Schmuttenmaer, "Carrier localization and cooling in dye-sensitized nanocrystalline titanium dioxide," *J. Phys. Chem. B* **106**, 11716-11719 (2002).
- [6] A. Pashkin, C. Kübler, H. Ehrke, R. Lopez, A. Halabica, R. F. Haglund, Jr., R. Huber and A. Leitenstorfer, "Ultrafast insulator-metal phase transition in VO₂ studied by multiterahertz spectroscopy," *Phys. Rev. B* **83**, 195120 (2011).
- [7] A. Pashkin, M. Porer, M. Beyer, K. W. Kim, A. Dubroka, C. Bernhard, X. Yao, Y. Dagan, R. Hackl, A. Erb, J. Demsar, R. Huber and A. Leitenstorfer, "Femtosecond Response of Quasiparticles and Phonons in Superconducting YBa₂Cu₃O_{7-δ} Studied by Wideband Terahertz Spectroscopy," *Phys. Rev. Lett.* **105** (2010).
- [8] R. Huber, F. Tauser, A. Brodschelm, M. Bichler, G. Abstreiter and A. Leitenstorfer, "How many-particle interactions develop after ultrafast excitation of an electron-hole plasma," *Nature* **414**, 286-289 (2001).
- [9] D. J. Cook and R. M. Hochstrasser, "Intense terahertz pulses by four-wave rectification in air," *Opt. Lett.* **25**, 1210-1212 (2000).
- [10] X. Xie, J. M. Dai and X. C. Zhang, "Coherent control of THz wave generation in ambient air," *Phys. Rev. Lett.* **96**, 075005 (2006).
- [11] J. Dai, X. Xie and X. C. Zhang, "Detection of broadband terahertz waves with a laser-induced plasma in gases," *Phys. Rev. Lett.* **97**, 103903 (2006).
- [12] F. C. Krebs, T. Tromholt and M. Jorgensen, "Upscaling of polymer solar cell fabrication using full roll-to-roll processing," *Nanoscale* **2**, 873-886 (2010).
- [13] D. G. Cooke, F. C. Krebs and P. U. Jepsen, "Direct observation of sub-100 fs mobile charge generation in a polymer/fullerene film," (submitted, 2011).